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Short Articles

Density, Viscosity, and Vapor Pressure of Phenyl Dichlorophosphite

Xian-Zhao Shao, Jun-Sheng Wu,* Gai-Qing Zhang, and Li-Sheng Wang

School of Chemical Engineering & the Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China

The density and viscosity of phenyl dichlorophosphite ($C_6H_5Cl_2OP$) over a temperature range of (293.27 to 423.25) K were measured. The vapor pressure of phenyl dichlorophosphite in the range of (363.25 to 480.79) K was measured by a static method. The density data were fitted to a second-order polynomial, and the viscosity data were fitted to the Andrade equation. The results of vapor pressure data were fitted to the Antoine equation. The density data and vapor pressure data of phenyl dichlorophosphite were compared with literature values. The absolute average deviations of density, viscosity, and vapor pressure fitting for phenyl dichlorophosphite are (0.16, 1.16, and 0.60) %, respectively.

Introduction

Phenyl dichlorophosphite $C_6H_5Cl_2OP$ (PDCP) is a useful reagent for forming a peptide link, presumably by activating either 2 equiv of carboxyl or amino groups.[1] Chiriac[2] used PDCP for the preparation of aromatic polyamides with relatively low inherent viscosity values. PDCP could also promote the reaction of amines and carbon dioxide through the activation of 2 mol of amines by the passage of carbon dioxide through a pyridine solution of PDCP and aniline.[3]

Although PDCP is not commercially available, its density, viscosity, and vapor pressure in a range of operating temperatures are very important for the design of industrial processes. This information has not been reported systematically in the literature. Up to now, the density value of PDCP at 293.15 K ($\rho = 1.353\ \text{g}\cdot\text{cm}^{-3}$)[4] was reported. The boiling temperatures of PDCP at 1.33 kPa[4] were reported in the literature.

In this paper, the density and viscosity of PDCP are presented in the range of (293.27 to 423.25) K, respectively, and the results of density were compared with the literature values. The vapor pressure of PDCP in the range of (363.25 to 480.79) K was measured by a static method and correlated to the Antoine equation. A comparison was made with reported values. The absolute average deviations of density, viscosity, and vapor pressure fitting for PDCP are (0.16, 1.16, and 0.60) %, respectively.

Experimental Section

Chemicals. PDCP was synthesized from phosphorus trichloride and phenol in our laboratory following the procedure described by Henry.[5] Then it was distilled under reduced pressure (1.33 kPa). The product was characterized by means of IR, ^{1}H NMR, and MS. The purity of PDCP after distillation was 97.75 % determined by a ^{31}P NMR test. The refractive index value was obtained at 20 °C on an Abbe model refractometer with an uncertainty of $\pm 0.0001 n_D$. The measured value was $n_D^{20} = 1.5613$, which agrees with the values in the literature ($n_D^{20} = 1.5886$,[4] $n_D^{20} = 1.5621$[6]). Ethylene glycol purchased from Beijing Chemical Reagent Company was an analytical reagent.

Table 1. Density of PDCP

T/K	ρ/g·cm^{-3}	$100\delta^a$	T/K	ρ/g·cm^{-3}	$100\delta^a$
293.27	1.3531	−0.385	373.06	1.2298	−0.071
303.25	1.3442	0.061	383.26	1.2141	0.048
313.20	1.3330	0.380	393.26	1.1965	−0.004
323.18	1.3204	0.577	403.66	1.1777	0.024
333.06	1.2934	−0.290	413.47	1.1612	0.072
343.20	1.2797	−0.112	423.25	1.1431	0.050
353.20	1.2622	−0.166			
363.18	1.2470	−0.042			

[a] $100\delta = 100(\rho - \rho_{\text{calcd}})\rho$.

Density Measurements. A 10 cm^3 pycnometer calibrated with deionized and double-distilled water was used for the measurements in the range of (293.27 to 323.18) K. The same pycnometer calibrated with ethylene glycol was used for the measurements in the range of (333.06 to 423.25) K. The mass was determined on an electronic balance with a precision of ± 0.1 mg. The picnometer was then immersed in a thermostat bath with temperature control precision of ± 0.1 K. The measured densities of PDCP are listed in Table 1. The densities of pure water and ethylene glycol are obtained from the literature.[7] The estimated uncertainty in density was $\pm 5 \cdot 10^{-4}\ \text{g}\cdot\text{cm}^{-3}$.

Viscosity Measurements. An Ubbelohde capillary viscometer was used to measure the viscosity. The capillary was calibrated (including a kinetic energy correction term) with pure water in the corresponding experimental temperature range. The kinematic viscosity is expressed as a function of two constants (k_1, k_2) and the flow time t

$$\nu = k_1 t - k_2 t \tag{1}$$

The kinematic viscosity ν for calibration was obtained from literature values of the absolute viscosity[8] and density. The capillary was 0.55 mm in diameter and 40 mm in length; therefore, the end correction could be neglected. The same viscometer was used for all measurements.

The temperature control setup used was identical to that used for density measurements described earlier. The flow time t

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* Corresponding author: E-mail: jswu@public3.bta.net.cn.

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Table 2. Viscosity of PDCP

T/K	η/mPa·S	$100\delta^a$	T/K	η/mPa·S	$100\delta^a$
293.27	2.206	2.768	373.06	0.721	−1.200
303.25	1.835	0.972	383.26	0.655	−1.323
313.20	1.554	−0.140	393.26	0.599	0.559
323.18	1.338	−0.566	403.66	0.542	0.221
333.06	1.155	−1.681	413.47	0.501	1.153
343.20	1.016	−1.396	423.25	0.467	2.381
353.20	0.900	−1.330			
363.18	0.800	−1.521			

[a] $100\delta = 100(\eta - \eta_{\text{calcd}})\eta$.

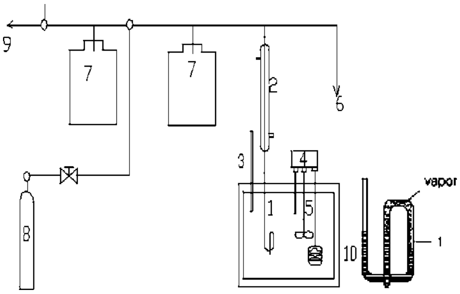

Figure 1. Apparatus for the measurement of vapor pressure: 1, equilibrium cell; 2, condenser; 3, temperature indicator; 4, thermoregulator; 5, agitator blade; 6, to mercury pressure gauge; 7, buffer bottle; 8, nitrogen cylinder; 9, to vacuum pump; 10, thermostat bath.

Table 3. Vapor Pressure Data of PDCP

T/K	p/kPa	$100\delta^a$	T/K	p/kPa	$100\delta^a$
363.25	1.47	−1.38	427.13	19.74	−0.65
368.85	1.93	−0.26	431.14	22.69	−0.18
373.36	2.39	0.20	434.75	25.54	−0.32
377.56	2.89	0.10	439.67	29.90	−0.43
381.85	3.49	0.06	443.56	33.78	−0.58
386.24	4.22	0.13	448.54	39.36	−0.72
390.85	5.11	0.09	453.36	45.46	−0.90
395.53	6.19	0.16	458.47	52.77	−1.09
398.76	7.04	0.17	461.57	57.67	−1.20
403.60	8.50	0.17	466.53	66.28	−1.40
408.48	10.23	0.18	471.06	75.05	−1.59
412.85	12.02	0.12	475.71	88.11	1.77
417.95	14.44	−0.04	480.79	101.33	2.19
422.05	16.67	−0.05			

[a] $100\delta = 100(p - p_{\text{calcd}})p$.

Table 4. Antoine Constants for PDCP

Antoine constants			temperature range	
A	B	C	T/K	100AAD
7.148	2317	−31.05	363.25 to 480.79	0.60

was recorded with a stopwatch of precision of 0.01 s. Each measurement was repeated 10 times and averaged as the final result. The measurement uncertainty was within ± 0.1 s (0.33 % at the high end of the temperature range). The density values used to convert kinematic viscosity to absolute values were calculated from the fitted equation. The measured viscosities of PDCP over a range of temperatures are listed in Table 2. The measured flow time was in the range of (80.51 to 214.05) s, and the estimated uncertainty in viscosity was within ± 0.5 %.

Vapor Pressure Measurements. The vapor pressure was measured by a static method. The apparatus setup is schematically shown in Figure 1. It consists of a temperature control and measurement system, a vacuum pump, and a pressure measurement system. An equilibrium cell with a U-type tube construction for the judgment of pressure balance, as shown in Figure 1, containing the liquid sample was immersed in the thermostat silicon oil bath. The temperature of the oil bath was controlled automatically by a YCC-16 intelligent controller to 0.1 K. In the pressure measurements, a U-type mercury pressure gauge was used, and the height difference was measured by a cathetometer. The measured pressures were corrected by a barometer. The accuracy of the pressure measurements was better than 0.013 kPa.

The apparatus setup had been tested by measuring the vapor pressure of pure water from (293.15 to 353.15) K and by comparing the results with literature values. The deviation between the experimental results and the literature values was within 0.2 %, which showed the apparatus to be reliable.

The equilibrium cell was made of thin-walled glass to aid the sample to reach rapid temperature equilibrium with the surrounding silicon oil bath. Before setting the equilibrium cell in the thermostat bath, it was necessary to degas the sample thoroughly. The liquid sample was degassed by repeated freeze evacuate−thaw cycles. After degassing, the equilibrium cell was immersed in the thermostat bath and connected to the vacuum system with a condenser in between.

Along with the evacuation process, the space in the U-type tube of the equilibrium cell was filled with pure vapor of the liquid sample. At each selected temperature, evacuation was conducted continuously until the liquid sample in the equilibrium cell began to boil, then the nitrogen gas was filled into the vacuum system carefully to adjust the system pressure to equal the vapor pressure of the sample by observing the liquid levels in the U-type tube of the equilibrium cell. The temperature and the pressure were recorded and corrected correspondingly. The operation was repeated seven to eight times at each temperature, and an averaged value was adopted. The maximum deviation between the individual measured values for each temperature was within ± 0.05 %. The vapor pressure measurement versus temperature was performed in every (3 to 6) K interval. The experimental vapor pressure data for PDCP in the range of (363.25 to 480.79) K are listed in Table 3.

Results and Discussion

Results. The measured data of the density, viscosity, and vapor pressure of PDCP were fitted to the following equations.

Density versus temperature was fitted to a second-order polynomial

$$\rho/\text{g}\cdot\text{cm}^{-3} = 1.686 - 7.430\cdot10^{-4}(T/\text{K}) - 1.279\cdot10^{-6}(T/\text{K}) \quad (2)$$

Viscosity versus temperature was fitted to the Andrade equation

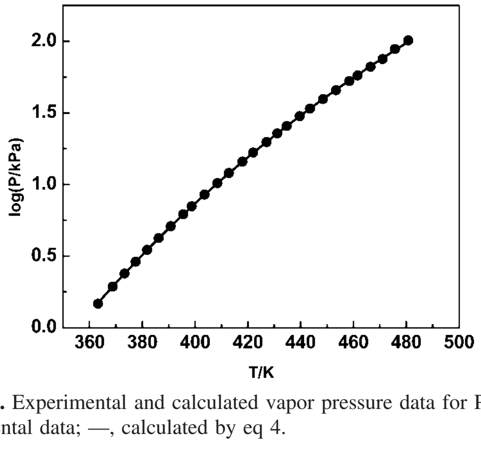

Figure 2. Experimental and calculated vapor pressure data for PDCP: ●, experimental data; —, calculated by eq 4.

$$\ln(\eta/\mathrm{mPa \cdot S}) = -4.277 + 1478/(T/\mathrm{K}) \tag{3}$$

Vapor pressure versus temperature was fitted to the Antoine equation

$$\log(p/\mathrm{kPa}) = A - \frac{B}{C + T/\mathrm{K}} \tag{4}$$

where p is the vapor pressure; T is the temperature; and A, B, and C are the Antoine constants.

The Antoine constants A, B, and C determined from least squares fitting and the absolute average deviation are listed in Table 4. A comparison of the vapor pressure obtained from the fitted equation and the measured data and the literature values is shown in Figure 2.

The absolute average deviation (AAD) of measured data from the fitted equation is defined as

$$\mathrm{AAD}(\rho) = \frac{1}{N}\Sigma|\rho_i - \rho_{i,\mathrm{calcd}}|/\rho_i \tag{5}$$

$$\mathrm{AAD}(\eta) = \frac{1}{N}\Sigma|\eta_i - \eta_{i,\mathrm{calcd}}|/\eta_i \tag{6}$$

$$\mathrm{AAD}(p) = \frac{1}{N}\Sigma|p_i - p_{i,\mathrm{calcd}}|/p_i \tag{7}$$

where the suffix calcd stands for the calculated values from fitted equations. The absolute average deviations of density, viscosity, and vapor pressure fitting for PDCP are (0.16, 1.16, and 0.60) %, respectively.

Discussion. The density of PDCP calculated from eq 2 at 293.15 K is 1.3582 $\mathrm{g \cdot cm^{-3}}$, which is in good agreement with the literature value 1.3531 $\mathrm{g \cdot cm^{-3}}$ at 293.15 K.[4] While the viscosity data over a temperature range of (293.27 to 423.25) K were fitted to the Andrade equation, no literature values are available.

Hudson[4] reported the boiling temperature of 90 °C at 1.33 kPa, and Gazizov[6] reported the boiling temperature of (90 to 92) °C at 1.47 kPa. Compared with the data of this work, 363.25 K (90.10 °C) at 1.47 kPa, they are in fairly good agreement.

Literature Cited

(1) Goldshmidt, S.; Obermeier, F. N-subsituierte amide der phosphprigen und phosphorsaure und a) deren reaction mit carbonsauren. *Ann.* **1954**, *24*, 588.

(2) Chiriac, C. I. Aromatic polyamides—A new direct condensation reaction. *Polym. Bull.* **1984**, *11*, 371.

(3) Yamazaki, N.; Tomioka, T.; Higashi, F. S. Studies on reaction of N-phosphonium salts of pyridines. 14 Wholly aromatic polyamides by direct polycondensation reaction by using phosphites in presence of metal-salts. *J. Polym. Sci., Part A: Polym. Chem.* **1975**, *13*, 1373.

(4) Hudson, H. R.; Kow, A.; Roberts, J. C. Quasiphosphonium intermediates. Part 3. Preparation, structure, and reactivity of alkoxyphosphonium halides in the reactions of neopentyl diphenylphosphinite, dineopentyl phenylphosphonite, and trineopentyl phosphite with halomethanes and the effect of phenoxy-substituents on the mechanism of alkyl-oxygen fission in Michaelis-Arbuzov reactions. *J. Chem. Soc. Perkin Trans. 2: Phys. Org. Chem.* **1983**, *9*, 1363–1368.

(5) Tolkmith, H. Aromatic phosphorodichloridites and phosphorodichloridothiates. I. Aryl phosphorodichloridites. *J. Org. Chem.* **1958**, *23*, 1682–1684.

(6) Gazizov, T. Kh.; Belyalov, R. U.; Pudovik, A. N. Reaction of phosphorous acid esters with phosphorus(III) chlorides. *Zh. Obshch. Khim.* **1983**, *53* (9), 1954−1957.

(7) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 63rd ed.; CRC Press: Boca Raton, FL, 1982−1983.

(8) Perry, R. H.; Green, D. W.; Malone, J. O. *Perry's Chemical Engineers Handbook*, 6th ed.; McGraw-Hill: New York, 1984.

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